Partially Fluorinated, Polyhedral Oligomeric Silsesquioxane-Functionalized (Meth)Acrylate Resists for 193 nm Bilayer Lithography

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The influence of partial fluorination on the lithographic performance of photoresists based on (meth)-acrylate terpolymers containing polyhedral oligomeric silsesquioxane (POSS) pendant groups is investigated in bilayer schemes for 193 nm lithography. For the first time the capability of POSS-functionalized resists for standard lithographic processing, including use of standard developer (0.26 N tetramethylammonium hydroxide) and industrial processing equipment is demonstrated. The optimized resists formulated exhibited high sensitivity (<10 mJ/cm^2) and potential for resolution performance comparable to mature 193 nm materials. The role of the fluorinated acid as a component in the terpolymer composition was crucial to the homogeneity of the resist material and its lithographic performance. Also, a photoacid generator (PAG) study revealed that the use of a highly hydrophobic PAG containing organic anion with a long fluorinated chain in the resist formulation improved further the homogeneity of the material and its lithographic performance. The adhesion of the highly fluorinated materials to the substrate is influenced by the type of polymeric underlayer used, whereas best results were obtained on a hard baked novolac polymer.

1. Introduction

The incessant improvement of the photoresist materials performance during the last 20 years has been one of the major factors that allowed the reduction of the integrated circuit dimensions according to the well-known Moore's law.[1−4] During the continuous reduction of the irradiation wavelength in the semiconductor industry from 436 nm gradually to 365 nm, to 248 nm, and recently to 193 nm, new resists were proposed at each new wavelength range that exploited to the highest degree the improved imaging properties of the advanced exposure tools. Today, the resolution achieved with the 193 nm lithography reaches 90 nm, while further decrease of the resolution to the 45 nm domain without decreasing the irradiation wavelength is considered feasible, mainly due to the advent of immersion lithography.[5,6]

Silicon containing polymers had been proposed from the early days of 193 nm lithography as one of the material classes that could combine improved lithographic performance and effective pattern transfer properties. In particular, Si-containing pendant groups such as the trimethylsilyl group had been incorporated into methacrylate backbones,[7] and very good lithographic behavior had been reported. Nevertheless, these materials were found to present very serious outgassing problems, related to the Si presence in the pendant group,[8] leading to subsequent lens damage, and for this reason they were abandoned. Thus, all-organic polymers have been used so far as the main components of the 193 nm resists, where the incorporation of cycloaliphatic functionalities, such as adamantane, norbornane, and so forth is applied to increase their etch resistance by increasing both their carbon content and carbon-ring content.[9] These alicyclic moieties have been either used as pendant groups in (meth)acrylate copolymers or have been incorporated directly into the polymer backbone, with a characteristic example being the norbornene−maleic anhydride alternating copolymer.[10,11] The (meth)-

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acrylate copolymer approach has been adopted by most groups, because of high glass-transition temperatures (T_g) and processing difficulties encountered in cycloolefine-based polymers.[12]

On the other hand, the interest for Si-containing resist materials was regenerated in the case of 157 nm lithography (which was considered for quite a few years as a possible successor of 193 nm lithography before the appearance of 193 nm immersion lithography) due to the low transparency of the majority of the resist materials in this wavelength,[13−15] because even C−C and C−H bonds absorb strongly at 157 nm. The materials proposed for 157 nm lithography were mainly based on two categories: fluorinated polymers and siloxanes−silsesquioxanes (SSQs), because C−F and Si−O bonds do not absorb strongly at 157 nm. In the first category, some fluorinated polymers with an alicyclic, methacrylic, or mixed alicyclic−methacrylic backbone[16−19] presented adequate transparency, but they usually suffered from low etch resistance and difficulty for optimizing lithographic performance, because poor adhesion, phase separation, and irregular development were often encountered. In the second category, the major effort was focused on SSQs, because siloxanes had the limitation of the negative tone imaging predominance. Specifically, SSQs with ladder-type structure were proposed[20] as exhibiting very good lithographic performance. On the other hand, outgassing problems,[8,21] due to the appearance of parallel photochemical pathways,[22] were also effectively addressed in these polymers by the increased number of nonabsorbing Si−O bonds and their network forming structure.

Recently, a new class of polymers functionalized with cage-type SSQs (polyhedral oligomeric silsesquioxane, POSS, moieties) was proposed for a variety of applications,[23] and they quickly drew the attention of the lithography community. Thus, (meth)acrylates with cyclopentyl-substituted POSS cages as pendant groups were initially proposed for X-ray and e-beam lithography.[24,25] Also, other POSS-functionalized resist materials were recently reported for 193 nm bilayer lithography.[26] Furthermore, the surface study of these POSS-functionalized polymeric films was an interesting issue because of the preferential population of POSS moieties at the surface of these films.[27,28] In previous work of our group (meth)acrylates with ethyl-substituted POSS moieties as pendant groups were proposed for 157 nm bilayer lithography.[29−33] Partial fluorination was also used in some cases as a means to reduce transparency at 157 nm. Promising high-resolution (100 nm) results were demonstrated with certain materials of this class, although difficulties for material formulation were often encountered because of inhomogeneity, phase separation, and nonreproducibility problems. On the other hand, nonstandard lithographic processing conditions (diluted tetramethylammonium hydroxide, TMAH, developers) had to be applied, limiting the interest for industrial exploitation.

In this paper, we investigate the impact of partial fluorination on the lithographic behavior of (meth)acrylates containing ethyl-substituted POSS cages as pendant groups. The resists are evaluated at 193 nm lithography following the new aim of the semiconductor industry to remain at 193 nm irradiation in light of the aforementioned evolutions. It is shown that partial fluorination has a clearly positive effect on both the homogeneity and the lithographic performance of these POSS-functionalized resists in such a way that a new 193 nm resist platform presenting very promising lithographic and etching characteristics and capability for standard lithographic processing has resulted.

2. Experimental Section

2.1. Materials. The monomers *tert*-butylmethacrylate (TBMA), 2-(trifluoromethyl)acrylic acid (TFMAA), and methacrylic acid (MAA), the initiator 2,2′-azobis(isobutyronitrile) (AIBN), and the solvents methyl isobutyl ketone (MIBK), tetrahydrofuran (THF),

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and methanol were purchased from Aldrich. The industry-standard developer of 0.26 N TMAH (trade name OPD5262) was supplied from Fujifilm. The monomer 3-(3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane-1-yl)propyl methacrylate or methacrylethyl-POSS (MAEPOSS) was supplied from Hybrid Plastics. The photoacid generators (PAGs), triphenylsulfonium triflate (TPSTF), triphenylsulfonium nonaflate (TPSNF), triphenylsulfonium perfluorooctylsulfonate (TPSPFOS), and triphenylsulfonium hexafluoroantimonate (TPSHFA), were obtained from Midori Kagaku. Solutions of polymers and various concentrations (5−30%, w/w, in solids) of PAGs in MIBK were prepared. The POSS-functionalized (meth)acrylates were synthesized according to conventional (AIBN-initiated) free-radical polymerization.[29,31] The fluorinated terpolymers were characterized with gel permeation chromatography (GPC), their number-average molecular weight (M_n) ranged between 1 000−10 000, and their polydispersity (D) ranged between 1.6 and 1.9. GPC analyses were performed on a Waters Breeze 1515 series liquid chromatograph with a differential refractometer (Waters 2410) as a detector.

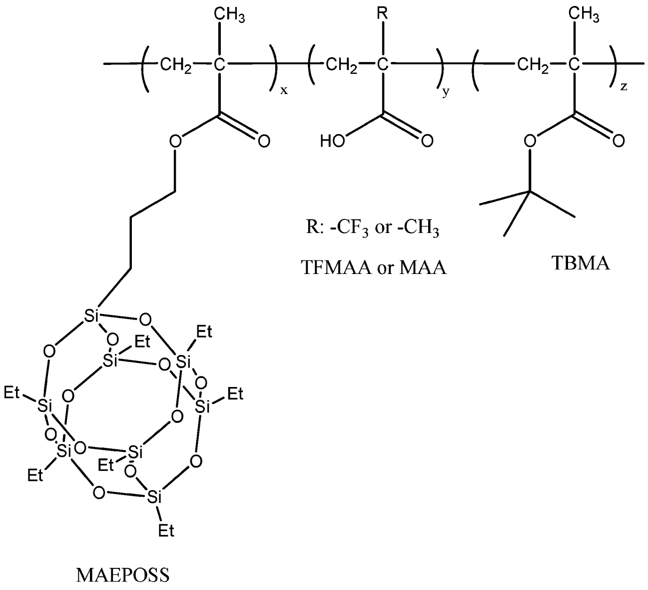
2.2. Physicochemical Characterization. UV−visible absorption spectra were taken on a quartz slide using a Perkin-Elmer UV−vis Lambda 40 spectrophotometer. Fourier transformed infrared (FTIR) transmittance spectra at a resolution of 4 cm^{-1} and 512 scans were recorded on a Si wafer using a Bruker, Tensor 27 instrument. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 500 MHz instrument with solvent $CDCl_3$ at 25 °C. Especially, the ^{13}C NMR spectrum was acquired using an inverse gated decoupling sequence and a relaxation delay of 12 s.

Modulated differential scanning calorimetry (MDSC) measurements at a heating rate of 5 °C/min and temperature modulation of ±0.80 °C every 60 s were recorded on a TA Instruments DSC 2920 model. In these measurements, T_g was determined at the inflection point of the glass transition presented in the reversing heat capacity curve.[34] MDSC measurements were always obtained from the second heating cycle, otherwise it is stated explicitly. Samples analyzed with the MDSC method were either powders produced from terpolymer synthesis or flakes from scrubbed terpolymer or resist films. The differentiation of the samples' derivation was done to investigate possible differences between the usually studied samples (powders from synthesis) and samples more close to the actual situation encountered in lithography (flakes from films). Prior to MDSC analysis, powders from synthesis were prebaked at 150 °C to remove the remaining solvents used in synthesis (THF, methanol, etc.), while flakes from scrubbed films were prebaked at 130 °C to remove the remaining casting solvent (MIBK).

Optical interferometry (OPTI) measurements were recorded on an experimental setup.[35−37] The OPTI method is applied for the in situ monitoring in a single run of glass transitions of thin polymeric films on Si wafers.The glass transition is monitored by the slope differentiation of the interference line, and T_g is obtained at the intersection of the two linear parts. OPTI measurements were obtained exclusively from the first heating cycle. Samples analyzed with the OPTI method were only films (∼100 nm thick). Prior to each OPTI measurement, the films were prebaked at 130 or 160 °C to remove the remaining casting solvent.

2.3. Lithographic Processing and Characterization. The underlayers used were TCU and TIS193 from Arch Chemicals. In a typical process the underlayers were ∼300 nm thick, baked at 200 °C for 2 min. The imaging layers were ∼100 nm thick, and both their post-applied bake (PAB) and their post-exposure bake (PEB) steps ranged between 130 and 160 °C. The imaging layers were exposed at broadband deep UV (DUV, wavelength range 220−280 nm) in a contact-printing mode, using a DUV Orial Hg−Xe 500 W exposure tool. Also, the imaging layers were exposed at 193 nm on IMEC's ASML PAS 5500/1100, a 193 nm scanner (NA 0.75, $\sigma = 0.89-0.57$). Lithographic characterization was carried out at (a) IMEL with an Ambios Technology XP-2 profilometer, LEO 440 Zeiss-Leica SEM instrument and Mitutoyo optical microscope, and (b) IMEC with a KLA-Tencor SEM, 8100XP instrument.

Scheme 1. Partially Fluorinated, POSS-Based (Meth)Acrylate Terpolymers



2.4. Plasma Etching. The etching equipment and conditions were the following: high-density plasma etcher MET by Alcatel, oxygen plasma, pressure 10 mTorr, ICP power 600 W, bias-100 V, oxygen flow 100 standard cm^3·min^{-1}, electrode temperature 25 °C, and He backside cooling for thermal contact between the wafer and the cooled electrode.

3. Results and Discussion

3.1. Synthesis of Terpolymers with Varying Fluorination Degree. *3.1.1. Selection and Role of Monomers in Terpolymer Composition.* The synthesis study was based on POSS-functionalized (meth)acrylates similar to the ones that our group had successfully applied for 157 nm lithography showing high contrast and good pattern transfer capability.[29−33] However, itaconic anhydride was not included as a component in the copolymer composition because of its known susceptibility to undergo hydrolysis reactions that limit resist self-life. Thus, POSS-functionalized (meth)acrylate terpolymers consisting of the monomers MAEPOSS, TBMA, and TFMAA (or MAA, if a nonfluorinated system was to be examined) were studied (Scheme 1). The first component was the ethyl-substituted POSS constituent (MAEPOSS), instead of the cyclopentyl-substituted one used by other groups,[24,25] because it gives higher etch resistance and lower surface roughness during pattern transfer according to our previous investigation.[29,32,38] Actually, the influence of POSS

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Table 1. Initial Feed Ratio (%, w/w) for the Synthesis of the Terpolymers Shown in Scheme 1

polymer	MAEPOSS	TBMA	TFMAA	MAA
F40	30	30	40	
F30	30	40	30	
F25	30	45	25	
F20	30	50	20	
F10	30	60	10	
F0	30	60		10

substituents on the lithographic characteristics of the resist, such as compatibility with the polymer matrix,[39] etch-resistance, and post-etching surface roughness,[31,38] has also been studied recently. The MAEPOSS percentage in the initial feed ratio was kept constant at 30% (w/w), because this is the minimum percentage that gives adequate etch resistance to a (meth)acrylate resist according to our previous study.[29] The second component was TBMA, because it provides the acid-labile *tert*-butyl group, necessary for the photoinduced solubility change.[4] The third component was the fluorinated acid TFMAA for two basic reasons. First, it is fluorinated, and its influence on the lithographic performance of the resist was the main objective of our investigation. Second, it is an acid, and an acidic component is mainly used to control the development kinetics of the resist in TMAH developers, but also it is used to improve polymer–PAG compatibility and resist adhesion. Alternatively, the nonfluorinated acid component (MAA) was used only for comparison with the fluorinated one (TFMAA). Therefore, for the needs of our study we synthesized a series of POSS-functionalized terpolymers by gradually reducing the initial feed percentage of TFMAA and finally replacing TFMAA with MAA (Table 1).

3.1.2. Composition of Terpolymers. The actual composition of the (meth)acrylate terpolymers synthesized was one of the issues studied. Thus, it was investigated if the composition of these terpolymers was similar to their initial feed ratio as it was previously reported.[24,29,31,40,41] The determination of the F30-terpolymer composition by a combination of ^{1}H NMR (Supporting Information, Figure S1a) and ^{13}C NMR spectroscopy (Supporting Information, Figure S1b, and Figure 1) showed that the actual composition of this polymer differs significantly from its initial feed ratio. Thus, the F30 terpolymer with initial feed ratio (%, w/w) of the monomers MAEPOSS/TBMA/TFMAA of 30:40:30 had composition (%, w/w) 50:28:21. The composition (%, w/w) was mainly determined by the quantitative proton-decoupled ^{13}C NMR spectrum without nuclear Overhauser effect (Figure 1). Thus, the molar ratio of the monomers TFMAA/(MAEPOSS + TBMA) was determined by the ratio of their integrated peaks at 171 ppm of $CO{-}CF_3$ and 177 ppm of $CO{-}CH_3$, respectively. Subsequently, the molar ratio of the monomers (MAEPOSS + TBMA)/MAEPOSS was determined by the ratio of the two integrated peaks at 177 ppm of $CO{-}CH_3$ and 4 ppm of the eight methylene groups located at the α-position to silicon, respectively. Consequently, in the actual composition of the F30 terpolymer the MAEPOSS percentage (%, w/w) was increased by 68% in relation to its nominal feed ratio, while the related percentages of TBMA and TFMAA were decreased by 30 and 29%, respectively. Actually, the reduction of the TFMAA percentage was expected, because TFMAA cannot be homopolymerized with conventional free-radical polymerization because of its electron deficiency; it can only be copolymerized with electron donor monomers, such as TBMA and MAEPOSS, forming random copolymers.[17,31] Conversely, the increase of the MAEPOSS percentage at the expense of TBMA was not expected, although the high compatibility of MAEPOSS with other methacrylate monomers was known,[24,40,41] and it cannot be explained either with the steric hindrance terms (POSS pendant group is more bulky than the *tert*-butyl one) or with the electronic terms (POSS pendant group is not electronically active). It seems probable that TFMAA, due to its extremely hydrophobic group $-CF_3$, prefers to be copolymerized with the more hydrophobic monomer MAEPOSS than the less hydrophobic TBMA.

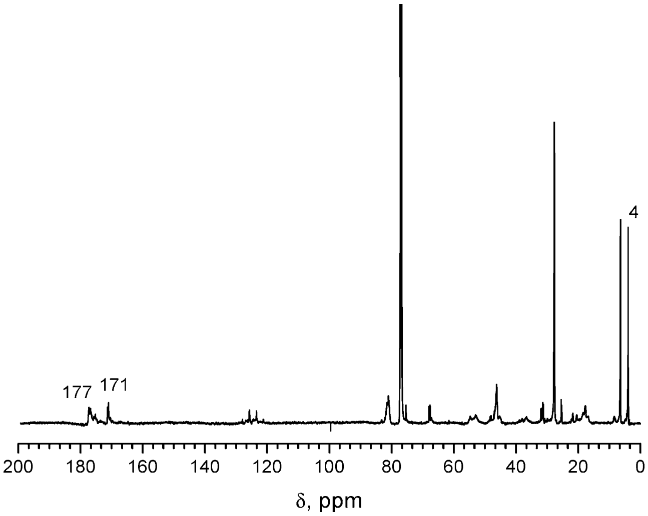

Figure 1. Quantitative ^{13}C NMR spectrum of the F30 terpolymer.

3.2. Basic Imaging Evaluation and Physicochemical Characterization. *3.2.1. Investigation of Imaging and Pattern Transfer Behavior.* Two resists based on one fluorinated, POSS-functionalized terpolymer (F10) and one nonfluorinated, POSS-functionalized terpolymer (F0) were primarily evaluated as far as their imaging and etching behavior are concerned. Thus, the two resist formulations (a) F10 with 25% (w/w) TPSNF and (b) F0 with 20% (w/w) TPSHFA were characterized with broadband DUV lithography and oxygen-plasma etching (Figure 2). The aim of the study was to examine if pattern transfer was feasible to allow the use of these materials, based on partially fluorinated, POSS-functionalized polymers, as bilayer resists. In Figure 2, it can be seen that features of 750 nm can be lithographically patterned, a resolution that is almost the best that could be achieved (minimum feature size 500 nm) under the exposure conditions applied. Furthermore, it is obvious that pattern

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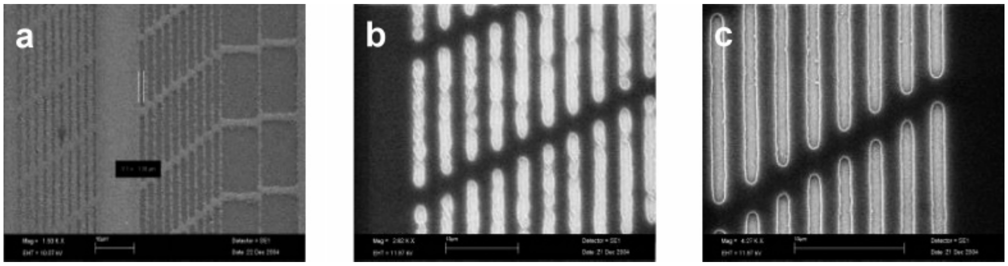

Figure 2. Pattern transfer results: SEM micrographs showing results obtained using broadband DUV contact printing and oxygen-plasma etching (on the TCU underlayer). Micrograph a is obtained after resist development, while micrograph b is obtained after the subsequent etching process of the F0-TPSHFA 20% (w/w) resist. Micrograph c is obtained after the etching process of the F10-TPSNF 25% (w/w) resist. Exposure dose and lithographic feature characteristics are as follows: (a) 100 s, 750 nm (1:1 and 2:1 lines/spaces, L/S), (b) 30 s, 1250 nm (1:2 L/S), and (c) 18 s, 1000 nm (1:2 L/S). (Thermal treatment: PAB/PEB 160 °C.)

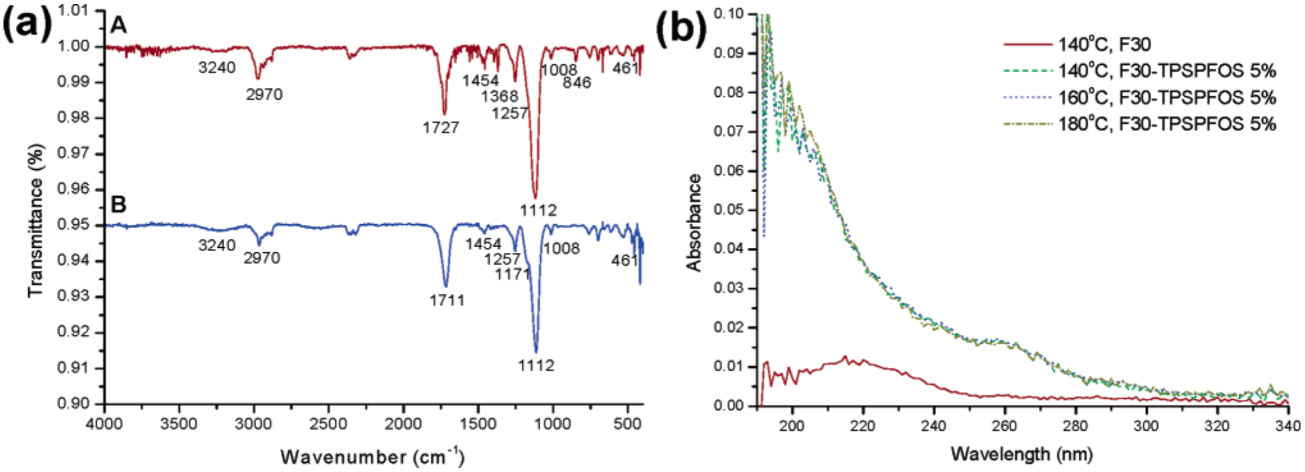

Figure 3. FTIR and UV−visible spectroscopy monitoring of the F30-TPSPFOS 5% (w/w) resist during lithographic processing. (a) FTIR spectra obtained (A) after PAB at 130 °C and (B) after the whole lithographic process: PAB at 130 °C, DUV exposure for 1000 s, and PEB at 130 °C. (b) UV spectra change of the above F30-based resist with increase of the PAB temperature and UV spectrum of the F30-terpolymer. (Film thickness ∼ 80 nm.)

transfer is feasible with oxygen-plasma etching, and etch resistance is adequate in accordance with previous observations for related materials.[29,31] Line-edge roughness (LER) was not studied because of the contact printing conditions used; however, our previous results for surface roughness[32,38] show very smooth surfaces after oxygen-plasma etching, and hint toward low LER.

Next, FTIR and UV−visible spectroscopy were used to monitor changes of an even more fluorinated resist, the F30-TPSPFOS 5% (w/w) resist, during lithographic processing (Figure 3). Specifically, the basic imaging reaction of this F30-based resist that is the acid-catalyzed cleavage of the *t*-butyl group of the terpolymer was studied with FTIR spectroscopy (Figure 3a). Although this reaction is known to take place during PEB, it was interesting to study it in a complicated system of a terpolymer-based resist. The following changes in the peaks observed in spectrum B (which is obtained after the whole lithographic process of PAB, DUV exposure, and PEB) in comparison with spectrum A (which is obtained after PAB) indicate the conversion of *tert*-butyl ester to carboxylic acid: increase of the 3240 cm^{-1} peak attributed to O−H stretching; decrease of the 2970 cm^{-1} peak of C−H stretching; shift of the 1727 cm^{-1} peak of C═O stretching to 1711 cm^{-1} due to acid formation; decrease of the 1454 cm^{-1} peak of C−H bending; complete elimination of the 1368 cm^{-1} peak of C−H bending; and appearance of a shoulder band at 1171 cm^{-1} assigned to C−O stretching, a band that was initially covered from the intense peak at 1112 cm^{-1} but now shifted to longer wavelengths due to acid formation. Furthermore, the possibility of TPSPFOS removal during PAB treatment of this resist film was investigated with UV−visible spectroscopy (Figure 3b). From this figure no change of the absorbance at 260 nm, which is entirely attributed to the aromatic rings of TPSPFOS, is observed, even at 180 °C (for comparison reasons the UV spectrum of the F30 terpolymer is also presented in this figure). Consequently, TPSPFOS was not removed from the resist film during PAB treatment, and the resist film remains photosensitive and homogeneous after that step.

The possibility for determining the fluorination degree (TFMAA percentage) of the synthesized terpolymers with FTIR spectroscopy was also investigated. Unfortunately, the FTIR spectra of two resists based on terpolymers with different fluorination degrees (F30 and F20 terpolymers), both formulated with 5% (w/w) TPSPFOS, were almost identical, because the C−F stretching peak that was to be studied was completely covered by the intense Si−O−Si peak at 1112 cm^{-1} (Supporting Information, Figure S2).

3.2.2. Thermal Transition Properties of Synthesized Terpolymers and Resist Formulations. T_g of both terpolymers and resist formulations was extensively studied mainly with the MDSC method, and secondarily with an interference-based, in situ method (OPTI method) proposed a few years ago.[35−37] T_g was studied for two basic reasons. First, T_g can function as an indirect index of material homogeneity, because the existence of a single T_g indicates homogeneity,

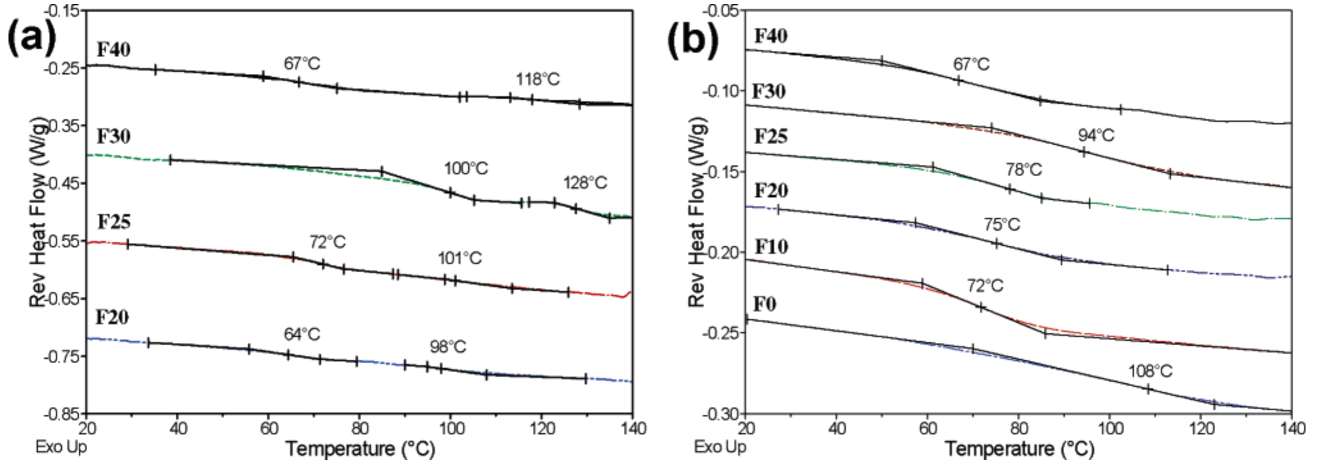

Figure 4. T_g measurements of (a) terpolymer samples from films (terpolymers: F40, F30, F25, F20) and (b) terpolymer powders (terpolymers: F40, F30, F25, F20, F10, F0), obtained with the MDSC method.

while the existence of two or more T_g values indicates inhomogeneity.[42,43] Second, T_g influences significantly the lithographic process, because it affects the selection of both PAB and PEB temperatures of the lithographic process. Consequently, the T_g study of both terpolymers and resists was expected to enlighten the influence of partial fluorination on the homogeneity of resist materials and generally on their lithographic behavior.

Initially, the effect of the fluorination degree on the homogeneity of the terpolymer samples was investigated with the MDSC method. It was found that all terpolymer samples (flakes) derived from films presented two T_g values (Figure 4a, and Supporting Information, Table S1), indicating that micro-phase separation or self-organization phenomena take place in these films. On the other hand, all initial terpolymer powders showed one T_g (Figure 4b, and Supporting Information, Table S1), indicating no self-organization phenomena. The possibility that phase separation phenomena observed with the MDSC method were not real and were created from the scrubbing of films during sample preparation is considered rather unlikely, because resist films with the addition of the appropriate PAG (TPSPFOS, see below) presented single T_g values and, thus, film homogeneity.

Subsequently, the effect of the fluorination degree on the homogeneity of the resist films was studied with the MDSC method. From resists based on terpolymers with increasing fluorination degree (F10 to F30) and formulated with 5% (w/w) TPSPFOS, only the F30-based resist presented one T_g and, thus, film homogeneity (the T_g measurements were obtained from the first heating cycle of MDSC analysis; Figure 5 and Supporting Information, Table S1). It seems that the increase of the fluorination degree, up to one of the F30-based resist, improved the homogeneity of the resists, probably by better mixing of the amphiphilic TFMAA component with the two hydrophobic components, MAE-POSS and TBMA. The fact that the F30-based resist is homogeneous, while the F10- and F20-based resists are inhomogeneous, is expected to have serious consequences in the lithographic performance, as it will be discussed in the relevant section below (Lithographic Evaluation at 193 nm).

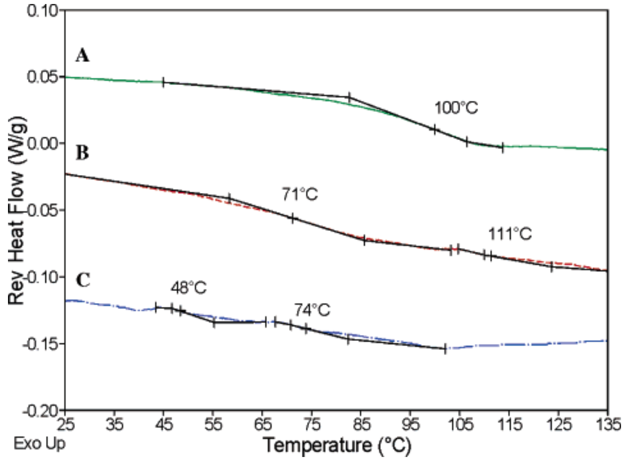

Figure 5. T_g measurements of resist films: (A) F30-TPSPFOS 5%, (B) F20-TPSPFOS 5%, and (C) F10-TPSPFOS 5% (w/w), obtained with MDSC method.

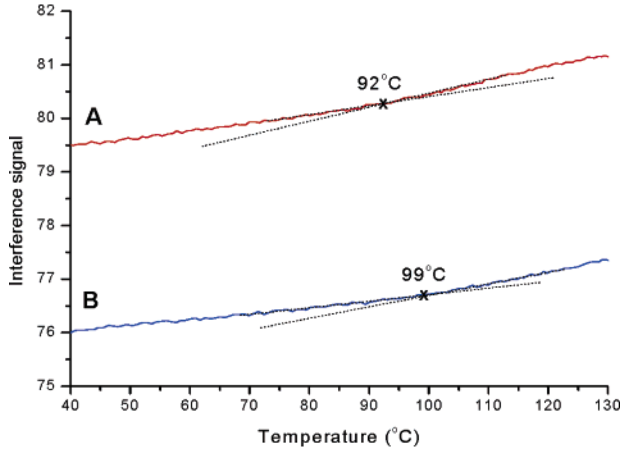

Figure 6. T_g measurements of the F30-TPSPFOS 5% (w/w) resist at two different PAB temperatures: (A) 130 °C and (B) 160 °C, obtained with the OPTI method.

Also, the effect of the PAB temperature on T_g of resist films was studied with the OPTI method (Figure 6 and Supporting Information, Table S1). It was noticed that T_g of the F30-TPSPFOS 5% (w/w) resist was increased with increase of the PAB temperature, as expected by better

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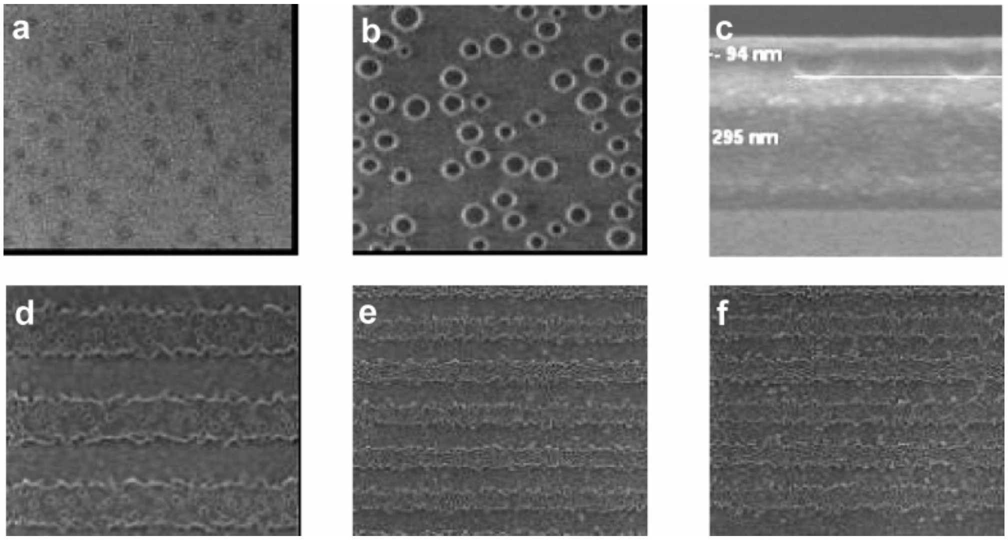

Figure 7. SEM micrographs of the F0-TPSHFA 20% (w/w) resist. (a) Top-down view of the resist film after coating. (b) Top-down view and (c) cross-sectional view of the resist film after development. (d−f) Top-down view of the lithographic results at 193 nm-exposure: 500 nm L/S resolution. Lithographic conditions (PAB/PEB temperature, exposure dose): (d) 120/120 °C, 2 mJ/cm^2, (e) 140/140 °C, 4 mJ/cm^2, and (f) 160/160 °C, 7.5 mJ/cm^2. (Film thickness 94 nm; TIS193 underlayer.)

removal of the casting solvent, free volume reduction, and better organization of the polymer chains. On the other hand, in some cases where two T_g values were observed with the MDSC method (most of the resist films and all of the terpolymer films, Supporting Information, Table S1), only one T_g was noticed with the OPTI method, indicating possibly inferior resolution capability of this method.

3.2.3. Influence of PAG on Lithographic Performance. The effect of PAGs with varying hydrophobicity and strength of generated acid on the lithographic performance of F30-based resists was studied, because these resists were proved more homogeneous from the thermal study. The PAGs examined were the following: TPSTF, TPSNF, TPSPFOS, and TPSHFA. These PAGs can be classified by the nature of their anion in two general categories: (a) PAGs with different fluorinated chain lengths of organic anion, one-carbon length (TPSTF), four-carbon length (TPSNF), and eight-carbon length (TPSPFOS), and (b) PAGs containing an inorganic anion (TPSHFA) versus PAGs containing an organic anion (TPSTF, TPSNF, TPSPFOS). From the lithographic results of this study (Supporting Information, Table S2) two important findings were concluded. (a) The F30-based resist formulated with the PAG containing an organic anion with the longest fluorinated chain (TPSPFOS) presented the best lithographic performance, and the decrease of the fluorinated chain length of the organic anion led to deterioration of the lithographic performance. In general, the best lithographic results followed the hydrophobicity sequence of PAGs: TPSPFOS > TPSNF > TPSTF. (b) The F30-based resist formulated with the PAG containing an inorganic anion (TPSHFA) was less sensitive by almost 1 order of magnitude than the one formulated with the PAGs containing an organic anion (Supporting Information, Table S2), even in an unusual high concentration (e.g., 30% TPSHFA vs 5%, w/w, TPSPFOS), which was used in an effort to investigate further this behavior. This finding was unexpected, because it is known that the acid generated from TPSHFA photolysis is probably the strongest known acid[44] and in any case comparable to the acid generated from TPSPFOS photolysis as it is known from comparison in other resist matrixes, for example, epoxy resists. However, it can be rationalized in terms of the hydrophobicity difference between TPSHFA and TPSPFOS. TPSHFA, resembling more an inorganic salt, is more hydrophilic than TPSPFOS, and thus it may reside in the more hydrophophilic sites (carboxyl groups) of the F30 terpolymer. On the other hand, TPSPFOS, because of its high hydrophobicity, is more evenly distributed inside this mainly hydrophobic polymer matrix. Thus, the F30-based resist formulated with 5% and 10% (w/w) TPSPFOS gave the best resolution achieved (500 nm) under the broadband DUV lithographic conditions applied. The formulation with 5% (w/w) TPSPFOS was finally selected, because it had a better process window: all three L/S ratios (2:1, 1:1, 1:2) of the 500 nm resolution were patterned for the specific lithographic process (PAB/PEB at 140 °C, DUV exposure for 60 s, development with standard TMAH solution) as it is presented in Supporting Information, Table S2.

3.3. Lithographic Evaluation at 193 nm. Two series of experiments were conducted using industry-standard, 193 nm-lithographic facilities. In the first series of experiments a nonfluorinated (F0-based) and a low fluorinated (F10-based) resist were evaluated. In these resists a high PAG concentration was used to increase their sensitivity, because this percentage was allowed from absorbance considerations. Thus, initially the F0-TPSHFA 20% (w/w) resist was examined. After resist coating, small microregions with the diameter ranging between 5 and 10 nm were detected in scanningn electron microscopy (SEM) micrographs (Figure 7a), indicating microphase separation inside the film and, thus, material inhomogeneity. These micro-areas were dissolved during the development so that the unexposed resist was full of pinholes as it can be seen in the SEM top/down and cross-sectional micrographs (Figure 7b,c). The poor

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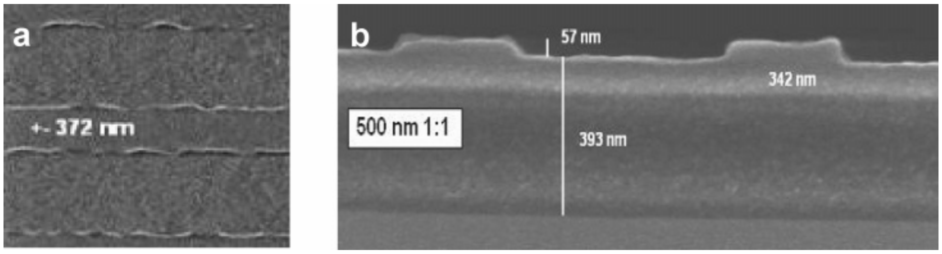

Figure 8. SEM micrographs of the F10-TPSNF 25% (w/w) resist. (a) Top-down view and (b) cross-sectional view of 500 nm L/S, at a 193 nm exposure dose of 8.6 mJ/cm^2. (Initial film thickness ∼ 90 nm; TCU underlayer.)

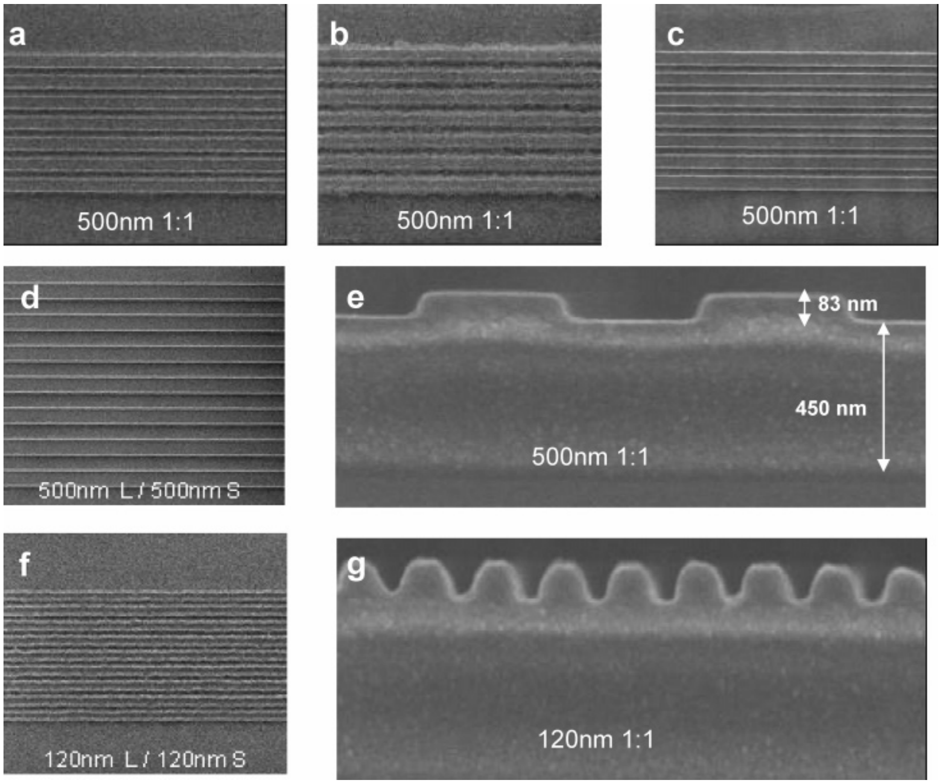

Figure 9. SEM micrographs of the F30-TPSPFOS 5% (w/w) resist. (a−e) Top-down and cross-sectional views of 500 nm L/S. (f, g) Top-down and cross-sectional view of 120 nm L/S. Lithographic conditions (PAB/PEB temperature and 193 nm exposure dose): (a) 140/140 °C, 2.4 mJ/cm^2, (b) 160/140 °C, 5 mJ/cm^2, (c) 135/100 °C, 4 mJ/cm^2, and (d−g) 135/100 °C, 8 mJ/cm^2. (Film thickness 85 nm, TCU underlayer.)

imaging quality limited the resolution to 500 nm L/S, whereas the simultaneous increase of the PAB and PEB temperature from 120 to 160 °C failed to improve the imaging quality (Figure 7d−f).

Subsequently, the F10-TPSNF 25% (w/w) resist was evaluated. No phase separation phenomena were detected in this resist film indicating material homogeneity. Nevertheless, the imaging behaviour of the resist was problematic. Thus, to remove completely the exposed resist areas an overdose was needed, which resulted in a decrease of the resist line width, that is, from 500 nm L/S on target 372 nm lines were obtained with the optimum dose of 8.6 mJ/cm^2 (Figure 8a). Furthermore, the cross-sectional SEM micrographs showed that considerable loss of resist thickness takes place during the development (Figure 8b). The resolution achieved was reduced to 350 nm L/S from 500 nmL/S on target.

During the lithographic evaluation at 193 nm the adhesion of the fluorinated resists was also proved to be a significant issue. It appears that the increase of the terpolymer fluorination reduced the adhesion of the resists. Thus, the F0-based resist was adequately adhered on the TIS193 underlayer, while the F10-based resist was insufficiently adhered on this underlayer, because the unexposed resist film was stripped even with the 1:300 water-diluted TMAH developer. On the other hand, the use of the novolac-based TCU underlayer improved the adhesion of the F10-based resist, as the unexposed resist film was not stripped with the standard TMAH developer. In fact, stripping of all the fluorinated resists, up to the F40-based resist, was avoided with the use of the TCU underlayer.

Having understood from the thermal study that the F30-TPSPFOS 5% (w/w) resist does not present microphase separation and having conducted successful lithographic processing of this resist at broadband DUV lithography, the second series of experiments at 193 nm lithography was concentrated on this resist. The initial processing conditions tried were the ones applied in preliminary lithographic evaluation at DUV (PAB/PEB at 140 °C, development with standard TMAH solution). Under these conditions the sensitivity was too high (<2 mJ/cm^2) at 193 nm exposure. The increase of the PAB temperature from 140 to 160 °C reduced the sensitivity of the resist, due to the resulted increase of T_g as revealed from the thermal study, but also reduced significantly its contrast (Figure 9a,b). On the other hand, the high decrease of the PEB temperature from 140 to 100 °C reduced the sensitivity but greatly improved the imaging quality. Representative results are shown in Figure 9c. Resolution down to 120 nm L/S at an exposure dose of 8 mJ/cm^2 is demonstrated (Figure 9d−g; development with a standard TMAH solution for 30 s).

4. Conclusions

In this paper, the effect of partial fluorination on the lithographic behavior of POSS-functionalized, (meth)acrylate-based resists was investigated in 193 nm bilayer lithography. Lithographic evaluation and thermal transition studies showed that the partial fluorination significantly improved the homogeneity of the resists, probably by better mixing of the amphiphilic fluorinated component (TFMAA) with the two hydrophobic components (MAEPOSS and TBMA) of the terpolymer, and finally enhanced their lithographic performance. TFMAA, because of its amphiphilicity, offers the possibility of synthesis of terpolymers with the same or even better lithographic characteristics than tetrapolymers. The homogeneity was further improved by the use of a highly hydrophobic PAG containing organic anion with long fluorinated chain (TPSPFOS) as proved from the PAG study. On the other hand, resolution similar to mature 193 nm materials, high sensitivity, and development in industry standard developers indicated promising lithographic performance of these highly fluorinated resists.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of the F30 terpolymer; FTIR spectra of the F30- and F20-based resists, both formulated with 5% (w/w) TPSPFOS; T_g measurements of terpolymers and some resist formulations obtained both with MDSC and the OPTI method; and lithographic results obtained from the PAG study of F30-based resists (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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